PATTERN FORMATION METHOD

BACKGROUND OF THE INVENTION

The present invention relates to a pattern formation method for use in fabrication process and the like for semiconductor devices.

In accordance with the increased degree of integration of semiconductor integrated circuits and downsizing of semiconductor devices, there are increasing demands for further rapid development of lithography technique. Currently, pattern formation is carried out through photolithography using exposing light of a mercury lamp, KrF excimer laser, ArF excimer laser or the like, and use of F_2 laser lasing at a shorter wavelength is being examined. However, since there remain a large number of problems in exposure systems and resist materials, photolithography using exposing light of a shorter wavelength has not been put to practical use.

In these circumstances, immersion lithography has been proposed for realizing further refinement of patterns by using conventional exposing light (M. Switkes and M. Rothschild, "Immersion lithography at 157 nm", J. Vac. Sci. Technol., B19, 2353 (2001)).

In the immersion lithography, a region in an exposure system sandwiched between a projection lens and a resist film formed on a wafer is filled with a solution having a refractive index **n**, and therefore, the NA (numerical aperture) of the exposure system has a value **n·NA**. As a result, the resolution of the resist film can be improved.

Now, a first conventional pattern formation method using the immersion lithography will be described with reference to FIGS. **8A** through **8D**.

First, a positive chemically amplified resist material having the following composition is prepared:

Base polymer: poly((norbornene-5-methylene-t-butylcarboxylate) – (maleic

anhydride)) (wherein norbornene-5-methylene-t-butylcarboxylate : maleic anhydride = 50 mol% : 50 mol%) ... 2 g

Acid generator: trifluorosulfonium triflate ... 0.06 g

Solvent: propylene glycol monomethyl ether acetate ... 20 g

Next, as shown in FIG. **8A**, the aforementioned chemically amplified resist material is applied on a substrate **1** so as to form a resist film **2** with a thickness of 0.35 μm.

Then, as shown in FIG. **8B**, while supplying water **3A** onto the resist film **2**, pattern exposure is carried out by irradiating the resist film **2** with exposing light **4** of ArF excimer laser with NA of 0.65 through a mask **5**. Although a projection lens for projecting the exposing light **4** having passed through the mask **5** on the surface of the resist film **2** is not shown in FIG. **8B**, a region sandwiched between the projection lens and the resist film **2** is filled with the water **3A**. Thus, an exposed portion **2a** of the resist film **2** becomes soluble in an alkaline developer because an acid is generated from the acid generator therein while an unexposed portion **2b** of the resist film **2** remains insoluble in an alkaline developer because no acid is generated from the acid generator therein.

After the pattern exposure, as shown in FIG. **8C**, the resist film **2** is baked with a hot plate at a temperature of 110°C for 60 seconds, and the resultant resist film is developed with a 2.38 wt% tetramethylammonium hydroxide developer (alkaline developer). In this manner, a resist pattern **6A** made of the unexposed portion **2b** of the resist film **2** can be obtained as shown in FIG. **8D**.

Next, a second conventional pattern formation method using the immersion lithography will be described with reference to FIGS. **9A** through **9D**.

First, a positive chemically amplified resist material having the following composition is prepared:

Base polymer: poly((norbornene-5-methylene-t-butylcarboxylate) – (maleic

anhydride)) (wherein norbornene-5-methylene-t-butylcarboxylate : maleic anhydride = 50 mol% : 50 mol%) ... 2 g

Acid generator: trifluorosulfonium triflate ... 0.06 g

Solvent: propylene glycol monomethyl ether acetate ... 20 g

Next, as shown in FIG. **9A**, the aforementioned chemically amplified resist material is applied on a substrate **1** so as to form a resist film **2** with a thickness of 0.20 μm.

Then, as shown in FIG. **9B**, while supplying perfluoropolyether **3B** onto the resist film **2**, pattern exposure is carried out by irradiating the resist film **2** with exposing light **4** of F_2 laser with NA of 0.60 through a mask **5**. Although a projection lens for projecting the exposing light **4** having passed through the mask **5** on the surface of the resist film **2** is not shown in FIG. **9B**, a region sandwiched between the projection lens and the resist film **2** is filled with the perfluoropolyether **3B**. Thus, an exposed portion **2a** of the resist film **2** becomes soluble in an alkaline developer because an acid is generated from the acid generator therein while an unexposed portion **2b** of the resist film **2** remains insoluble in an alkaline developer because no acid is generated from the acid generator therein.

After the pattern exposure, as shown in FIG. **9C**, the resist film **2** is baked with a hot plate at a temperature of 100°C for 60 seconds, and the resultant resist film is developed with a 2.38 wt% tetramethylammonium hydroxide developer (alkaline developer). In this manner, a resist pattern **6B** made of the unexposed portion **2b** of the resist film **2** can be obtained as shown in FIG. **9D**.

As shown in FIGS. **8D** and **9D**, however, each of the resist patterns **6A** and **6B** formed by the first and second conventional pattern formation methods is in a defective T-top shape.

Since the positive chemically amplified resist material is used in each of the first and second conventional pattern formation methods, the resist pattern **6A** or **6B** is in the T-

top shape. When a negative chemically amplified resist material is used instead, the resultant resist pattern is in a cross-section with round shoulders.

When a resist pattern in such a defective shape is used for etching a target film, the resultant pattern is also in a defective shape, which disadvantageously lowers the productivity and the yield in the fabrication process for semiconductor devices.

SUMMARY OF THE INVENTION

In consideration of the aforementioned conventional problem, an object of the invention is forming a resist pattern in a good shape by the immersion lithography.

In order to achieve the object, the first pattern formation method of this invention includes the steps of forming a resist film made from a chemically amplified resist material; performing pattern exposure by selectively irradiating the resist film with exposing light while supplying, onto the resist film, a solution that includes an acid generator for generating an acid through irradiation with light; and forming a resist pattern by developing the resist film after the pattern exposure.

In the first pattern formation method, the pattern exposure is performed with the acid generator supplied onto the resist film. Therefore, even when an acid generated from an acid generator included in the chemically amplified resist material diminishes in quantity because it flows into the solution or is deactivated due to the influence of the solution, the diminished quantity of the acid can be covered by an acid generated from the acid generator included in the solution. Accordingly, deactivation of the acid in an exposed portion of the resist film can be avoided, and hence, the resist pattern can be formed in a good shape. The acid generated from the acid generator included in the solution is also supplied to an unexposed portion of the resist film. However, when the quantity of the acid generated from the acid generator included in the solution is set to be

lower than the threshold value of the quantity of the acid necessary for changing the solubility in a developer of the unexposed portion of the resist film, the acid supplied to the unexposed portion causes no problem.

The second pattern formation method of this invention includes the steps of forming a resist film made from a chemically amplified resist material; performing pattern exposure by selectively irradiating the resist film with exposing light while supplying, onto the resist film, a solution including an acid; and forming a resist pattern by developing the resist film after the pattern exposure.

In the second pattern formation method, the pattern exposure is performed with the acid supplied onto the resist film. Therefore, even when an acid generated from an acid generator included in the chemically amplified resist material diminishes in quantity because it flows into the solution or is deactivated due to the influence of the solution, the diminished quantity of the acid can be covered by the acid included in the solution. Accordingly, the deactivation of the acid in an exposed portion of the resist film can be avoided, and hence, the resist pattern can be formed in a good shape. The acid included in the solution is also supplied to an unexposed portion of the resist film. However, when the quantity of the acid included in the solution is set to be lower than the threshold value of the quantity of the acid necessary for changing the solubility in a developer of the unexposed portion of the resist film, the acid supplied to the unexposed portion causes no problem.

The third pattern formation method of this invention includes the steps of forming a resist film made from a chemically amplified resist material; forming, on the resist film, a water-soluble film including an acid generator for generating an acid through irradiation with light; performing pattern exposure by selectively irradiating the resist film with exposing light while supplying a nonaqueous solution onto the water-soluble film; and

forming a resist pattern by developing the resist film after the pattern exposure.

In the third pattern formation method, the water-soluble film including the acid generator is formed on the resist film. Therefore, even when an acid generated from an acid generator included in the chemically amplified resist material diminishes in quantity because it flows into the nonaqueous solution or is deactivated due to the influence of the nonaqueous solution, the diminished quantity of the acid can be covered by an acid generated from the acid generator included in the water-soluble film. Accordingly, the deactivation of the acid in an exposed portion of the resist film can be avoided, and hence, the resist pattern can be formed in a good shape. In the third pattern formation method, the acid generated from the acid generator included in the water-soluble film is supplied substantially merely to an exposed portion of the resist film, and therefore, a problem that an unwanted acid is supplied to an unexposed portion of the resist film can be substantially avoided. Also, although the water-soluble film is formed on the resist film in the third pattern formation method, the water-soluble film is never dissolved because the immersion lithography is performed by using the nonaqueous solution.

The fourth pattern formation method of this invention includes the steps of forming a resist film made from a chemically amplified resist material; forming, on the resist film, a water-soluble film including an acid; performing pattern exposure by selectively irradiating the resist film with exposing light while supplying a nonaqueous solution onto the water-soluble film; and forming a resist pattern by developing the resist film after the pattern exposure.

In the fourth pattern formation method, the water-soluble film including the acid is formed on the resist film. Therefore, even when an acid generated from an acid generator included in the chemically amplified resist material diminishes in quantity because it flows into the nonaqueous solution or is deactivated due to the influence of the

nonaqueous solution, the diminished quantity of the acid can be covered by the acid included in the water-soluble film. Accordingly, the deactivation of the acid in an exposed portion of the resist film can be avoided, and hence, the resist pattern can be formed in a good shape. The acid included in the water-soluble film is also supplied to an unexposed portion of the resist film. However, when the quantity of the acid included in the water-soluble film is set to be lower than the threshold value of the quantity of the acid necessary for changing the solubility in a developer of the unexposed portion of the resist film, the acid supplied to the unexposed portion causes no problem. Also, although the water-soluble film is formed on the resist film in the fourth pattern formation method, the water-soluble film is never dissolved because the immersion lithography is performed by using the nonaqueous solution.

The fifth pattern formation method of this invention includes the steps of forming a resist film made from a chemically amplified resist material; forming, on the resist film, a water-soluble film including an acid polymer; performing pattern exposure by selectively irradiating the resist film with exposing light while supplying a nonaqueous solution onto the water-soluble film; and forming a resist pattern by developing the resist film after the pattern exposure.

In the fifth pattern formation method, the water-soluble film including the acid polymer is formed on the resist film. Therefore, even when an acid generated from an acid generator included in the chemically amplified resist material diminishes in quantity because it flows into the nonaqueous solution or is deactivated due to the influence of the nonaqueous solution, the diminished quantity of the acid can be covered by an acid generated from the acid polymer included in the water-soluble film. Accordingly, the deactivation of the acid in an exposed portion of the resist film can be avoided, and hence, the resist pattern can be formed in a good shape. The acid polymer included in the water-

soluble film is also supplied to an unexposed portion of the resist film. However, when the quantity of the acid polymer included in the water-soluble film is set to be lower than the threshold value of the quantity of the acid necessary for changing the solubility in a developer of the unexposed portion of the resist film, the acid supplied to the unexposed portion causes no problem. Also, although the water-soluble film is formed on the resist film in the fifth pattern formation method, the water-soluble film is never dissolved because the immersion lithography is performed by using the nonaqueous solution.

In the first or second pattern formation method, the solution supplied onto the resist film is preferably water.

When water having a high refractive index is used as the solution, a value **n·NA** can be definitely large.

In the first or second pattern formation method, the solution supplied onto the resist film is preferably perfluoropolyether.

When perfluoropolyether is used as the solution, even when a water-soluble film is formed on the resist film, the water-soluble film can be prevented from being dissolved in the solution.

In the third, fourth or fifth pattern formation method, the nonaqueous solution supplied onto the resist film can be perfluoropolyether.

In the first or third pattern formation method, the acid generator can be an onium salt.

In the second or fourth pattern formation method, the acid can be acetic acid.

In the third or fourth pattern formation method, the water-soluble film can be a polyvinyl alcohol film or a polyvinyl pyrrolidone film.

In the fifth pattern formation method, the acid polymer can be polyacrylic acid or polystyrene sulfonic acid.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** is a partial cross-sectional view of an exposure system commonly used in preferred embodiments of the invention;

FIGS. **2A**, **2B**, **2C** and **2D** are cross-sectional views for showing procedures in a pattern formation method according to Embodiment 1 of the invention;

FIGS. **3A**, **3B**, **3C** and **3D** are cross-sectional views for showing procedures in a pattern formation method according to Embodiment 2 of the invention;

FIGS. **4A**, **4B**, **4C** and **4D** are cross-sectional views for showing procedures in a pattern formation method according to Embodiment 3 of the invention;

FIGS. **5A**, **5B**, **5C** and **5D** are cross-sectional views for showing procedures in a pattern formation method according to Embodiment 4 of the invention;

FIGS. **6A**, **6B**, **6C** and **6D** are cross-sectional views for showing procedures in a pattern formation method according to Embodiment 5 of the invention;

FIGS. **7A**, **7B**, **7C** and **7D** are cross-sectional views for showing procedures in a pattern formation method according to Embodiment 6 of the invention;

FIGS. **8A**, **8B**, **8C** and **8D** are cross-sectional views for showing procedures in a first conventional pattern formation method; and

FIGS. **9A**, **9B**, **9C** and **9D** are cross-sectional views for showing procedures in a second conventional pattern formation method.

DETAILED DESCRIPTION OF THE INVENTION

Pattern formation methods according to preferred embodiments of the invention will now be described, and first of all, an exposure system used in each embodiment will be described with reference to FIG. **1**.

As shown in FIG. **1**, a projection lens **12** of the exposure system is provided above a resist film **11** formed on a semiconductor substrate **10**, and a solution storage **14** for storing a solution **13** (with a refractive index **n**) is provided between the projection lens **12** and the resist film **11**. The solution storage **14** is provided with an inlet **14a** for allowing the solution **13** to flow into and an outlet **14b** for allowing the solution **13** to flow out of the solution storage **14**, and the solution **13** having flown into the solution storage **14** through the inlet **14a** is temporarily stored in the solution storage **14** and then flows out through the outlet **14b**. Accordingly, exposing light **15** passes through a mask **16** having a desired pattern, is then projected by the projection lens **12** so as to reach the surface of the resist film **11** through the solution **13**. Therefore, the numerical aperture **NA** of the exposing light that reaches the surface of the resist film **11** through the solution **13** has a value **n** times as large as that attained when the exposing light reaches without passing through the solution **13**.

EMBODIMENT 1

A pattern formation method according to Embodiment 1 of the invention will now be described with reference to FIGS. **2A** through **2D**.

First, a positive chemically amplified resist material having the following composition is prepared:

Base polymer: poly((norbornene-5-methylene-t-butylcarboxylate) – (maleic anhydride)) (wherein norbornene-5-methylene-t-butylcarboxylate : maleic anhydride = 50 mol% : 50 mol%) ... 2 g

Acid generator: trifluorosulfonium triflate ... 0.06 g

Solvent: propylene glycol monomethyl ether acetate ... 20 g

Next, as shown in FIG. **2A**, the aforementioned chemically amplified resist material is applied on a substrate **101** so as to form a resist film **102** with a thickness of

0.35 μm.

Then, as shown in FIG. **2B**, while supplying, between a projection lens **106** and the resist film **102**, water **103** (having a refractive index **n** of 1.44) that includes 3 wt% of triphenylsulfonium nonaflate (an onium salt), that is, an acid generator, and is circulated and temporarily stored in the solution storage **14** (shown in FIG. **1**), pattern exposure is carried out by irradiating the resist film **102** with exposing light **104** of ArF excimer laser with NA of 0.65 through a mask not shown. Thus, an exposed portion **102a** of the resist film **102** becomes soluble in an alkaline developer because an acid is generated from the acid generator therein while an unexposed portion **102b** of the resist film **102** remains insoluble in an alkaline developer because no acid is generated from the acid generator therein.

After the pattern exposure, as shown in FIG. **2C**, the resist film **102** is baked with a hot plate at a temperature of 110°C for 60 seconds, and the resultant resist film is developed with a 2.38 wt% tetramethylammonium hydroxide developer (alkaline developer). In this manner, a resist pattern **105** made of the unexposed portion **102b** of the resist film **102** and having a line width of 0.09 μm can be formed in a good shape as shown in FIG. **2D**.

In Embodiment 1, since the pattern exposure is carried out while supplying the water **103** that includes the acid generator onto the resist film **102**, even when the acid generated from the acid generator in the exposed portion **102a** of the resist film **102** flows into the water **103** and diminishes in quantity, the diminished quantity of the acid is covered by an acid generated from the acid generator included in the water **103**. Therefore, deactivation of the acid in the exposed portion **102a** of the resist film **102** can be avoided, so that the resist pattern **105** can be formed in a good shape.

Although the acid generated from the acid generator included in the water **103** is

also supplied to the unexposed portion **102b** of the resist film **102**, the quantity of the acid generator included in the water **103** is small, and therefore, the unexposed portion **102b** of the resist film **102** remains insoluble in an alkaline developer.

Although the acid generator is included in the water **103** in Embodiment 1, approximately 3 wt% of acetic acid may be included instead in the water **103** as an acid. In this case, although the acetic acid included in the water **103** is also supplied to the unexposed portion **102b** of the resist film **102**, the quantity of acetic acid included in the water **103** is small, and therefore, the unexposed portion **102b** of the resist film **102** remains insoluble in an alkaline developer.

Alternatively, the acid included in the water **103** may be acrylic acid, formic acid or the like instead of acetic acid.

EMBODIMENT 2

A pattern formation method according to Embodiment 2 of the invention will now be described with reference to FIGS. **3A** through **3D**.

First, a negative chemically amplified resist material having the following composition is prepared:

Base polymer: poly((norbornene-5-methylenecarboxylate) – (maleic anhydride)) (wherein norbornene-5-methylenecarboxylate : maleic anhydride = 50 mol% : 50 mol%) ... 2 g

Crosslinking agent: 1,3,5-N-(trihydroxymethyl)melamine ... 0.7 g

Acid generator: trifluorosulfonium triflate ... 0.06 g

Solvent: propylene glycol monomethyl ether acetate ... 20 g

Next, as shown in FIG. **3A**, the aforementioned chemically amplified resist material is applied on a substrate **201** so as to form a resist film **202** with a thickness of 0.35 μm.

Then, as shown in FIG. **3B**, while supplying, between a projection lens **206** and the resist film **202**, water **203** that includes 3 wt% of triphenylsulfonium nonaflate (an onium salt), that is, an acid generator, and is circulated and temporarily stored in the solution storage **14** (shown in FIG. **1**), pattern exposure is carried out by irradiating the resist film **202** with exposing light **204** of ArF excimer laser with NA of 0.65 through a mask not shown. Thus, an exposed portion **202a** of the resist film **202** becomes insoluble in an alkaline developer due to the function of the crosslinking agent because an acid is generated from the acid generator therein while an unexposed portion **202b** of the resist film **202** remains soluble in an alkaline developer because no acid is generated from the acid generator therein.

After the pattern exposure, as shown in FIG. **3C**, the resist film **202** is baked with a hot plate at a temperature of 120°C for 90 seconds, and the resultant resist film is developed with a 2.38 wt% tetramethylammonium hydroxide developer (alkaline developer). In this manner, a resist pattern **205** made of the exposed portion **202a** of the resist film **202** and having a line width of 0.09 μm can be formed in a good shape as shown in FIG. **3D**.

In Embodiment 2, since the pattern exposure is carried out while supplying the water **203** that includes the acid generator onto the resist film **202**, even when the acid generated from the acid generator in the exposed portion **202a** of the resist film **202** flows into the water **203** and diminishes in quantity, the diminished quantity of the acid is covered by an acid generated from the acid generator included in the water **203**. Therefore, deactivation of the acid in the exposed portion **202a** of the resist film **202** can be avoided, so that the resist pattern **205** can be formed in a good shape.

Although the acid generated from the acid generator included in the water **203** is also supplied to the unexposed portion **202b** of the resist film **202**, the quantity of the acid

generator included in the water **203** is small, and therefore, the unexposed portion **202b** of the resist film **202** remains soluble in an alkaline developer.

Although the acid generator is included in the water **203** in Embodiment 2, approximately 3 wt% of acetic acid may be included instead in the water **203** as an acid. In this case, although the acetic acid included in the water **203** is also supplied to the unexposed portion **202b** of the resist film **202**, the quantity of the acetic acid included in the water **203** is small, and therefore, the unexposed portion **202b** of the resist film **202** remains soluble in an alkaline developer.

Alternatively, the acid included in the water **203** may be acrylic acid, formic acid or the like instead of acetic acid.

EMBODIMENT 3

A pattern formation method according to Embodiment 3 of the invention will now be described with reference to FIGS. **4A** through **4D**.

First, a positive chemically amplified resist material having the following composition is prepared:

Base polymer: poly((norbornene-5-methylene-t-butylcarboxylate) – (maleic anhydride)) (wherein norbornene-5-methylene-t-butylcarboxylate : maleic anhydride = 50 mol% : 50 mol%) ... 2 g

Acid generator: trifluorosulfonium triflate ... 0.06 g

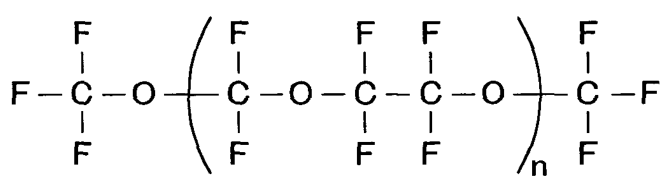
Solvent: propylene glycol monomethyl ether acetate ... 20 g

Next, as shown in FIG. **4A**, the aforementioned chemically amplified resist material is applied on a substrate **301** so as to form a resist film **302** with a thickness of 0.20 μm.

Then, as shown in FIG. **4B**, while supplying, between a projection lens **306** and the resist film **302**, a nonaqueous solution **303** of perfluoropolyether (having a refractive

index of 1.37) that is represented by Chemical Formula 1, includes 5 wt% of triphenylsulfonium nonaflate (an onium salt), that is, an acid generator, and is circulated and temporarily stored in the solution storage **14** (shown in FIG. **1**), pattern exposure is carried out by irradiating the resist film **302** with exposing light **304** of F_2 laser with NA of 0.60 through a mask not shown. Thus, an exposed portion **302a** of the resist film **302** becomes soluble in an alkaline developer because an acid is generated from the acid generator therein while an unexposed portion **302b** of the resist film **302** remains insoluble in an alkaline developer because no acid is generated from the acid generator therein.

Chemical Formula 1:



After the pattern exposure, as shown in FIG. **4C**, the resist film **302** is baked with a hot plate at a temperature of 100°C for 60 seconds, and the resultant resist film is developed with a 2.38 wt% tetramethylammonium hydroxide developer (alkaline developer). In this manner, a resist pattern **305** made of the unexposed portion **302b** of the resist film **302** and having a line width of 0.06 μm can be formed in a good shape as shown in FIG. **4D**.

In Embodiment 3, since the pattern exposure is carried out while supplying the nonaqueous solution **303** that includes the acid generator onto the resist film **302**, even when the acid generated from the acid generator in the exposed portion **302a** of the resist film **302** flows into the nonaqueous solution **303** and diminishes in quantity, the diminished

quantity of the acid is covered by an acid generated from the acid generator included in the nonaqueous solution **303**. Therefore, deactivation of the acid in the exposed portion **302a** of the resist film **302** can be avoided, so that the resist pattern **305** can be formed in a good shape.

Although the acid generated from the acid generator included in the nonaqueous solution **303** is also supplied to the unexposed portion **302b** of the resist film **302**, the quantity of the acid generator included in the nonaqueous solution **303** is small, and therefore, the unexposed portion **302b** of the resist film **302** remains insoluble in an alkaline developer.

Although the acid generator included in the nonaqueous solution **303** is triphenylsulfonium nonaflate in Embodiment 3, the acid generator may be a sulfone compound such as bis(phenylsulfonyl)methane; a sulfonate compound such as 2,6-dinitrobenzyltosylate or pyrogallol trimesylate; or a sulfonimide compound such as N-(trifluoromethylsulfonyloxy)succinimide, N-(trifluoromethylsulfonyloxy)phthalimide or N-(trifluoromethylsulfonyloxy)diphenylmaleimide instead.

Although the acid generator is included in the nonaqueous solution **303** in Embodiment 3, approximately 8 wt% of acetic acid may be included instead in the nonaqueous solution **303** as an acid. In this case, although the acetic acid included in the nonaqueous solution **303** is also supplied to the unexposed portion **302b** of the resist film **302**, the quantity of the acetic acid included in the nonaqueous solution **303** is small, and therefore, the unexposed portion **302b** of the resist film **302** remains insoluble in an alkaline developer.

Alternatively, the acid included in the nonaqueous solution **303** may be acrylic acid, formic acid or the like instead of acetic acid.

EMBODIMENT 4

A pattern formation method according to Embodiment 4 of the invention will now be described with reference to FIGS. **5A** through **5D**.

First, a positive chemically amplified resist material having the following composition is prepared:

Base polymer: poly((norbornene-5-methylene-t-butylcarboxylate) – (maleic anhydride)) (wherein norbornene-5-methylene-t-butylcarboxylate : maleic anhydride = 50 mol% : 50 mol%) ... 2 g

Acid generator: trifluorosulfonium triflate ... 0.06 g

Solvent: propylene glycol monomethyl ether acetate ... 20 g

Next, as shown in FIG. **5A**, the aforementioned chemically amplified resist material is applied on a substrate **401** so as to form a resist film **402** with a thickness of 0.20 μm. Thereafter, a water-soluble film **403** made of a polyvinyl alcohol film including 5 wt% of triphenylsulfonium triflate, that is, an acid generator, is formed on the resist film **402**.

Then, as shown in FIG. **5B**, while supplying, between a projection lens **407** and the water-soluble film **403**, a nonaqueous solution **404** of perfluoropolyether that is circulated and temporarily stored in the solution storage **14** (shown in FIG. **1**), pattern exposure is carried out by irradiating the resist film **402** and the water-soluble film **403** with exposing light **405** of F_2 laser with NA of 0.60 through a mask not shown. Thus, an exposed portion **402a** of the resist film **402** becomes soluble in an alkaline developer because an acid is generated from the acid generator therein while an unexposed portion **402b** of the resist film **402** remains insoluble in an alkaline developer because no acid is generated from the acid generator therein.

After the pattern exposure, as shown in FIG. **5C**, the resist film **402** is baked with a hot plate at a temperature of 100°C for 60 seconds, and the resultant resist film is

developed with a 2.38 wt% tetramethylammonium hydroxide developer (alkaline developer). Thus, the water-soluble film **403** and the exposed portion **402a** of the resist film **402** are dissolved in the alkaline developer. In this manner, a resist pattern **406** made of the unexposed portion **402b** of the resist film **402** and having a line width of 0.09 μm can be formed in a good shape as shown in FIG. **5D**.

In Embodiment 4, since the pattern exposure is carried out after forming the water-soluble film **403** including the acid generator on the resist film **402**, even when the acid generated from the acid generator in the exposed portion **402a** of the resist film **402** flows into the nonaqueous solution **404** and diminishes in quantity, the diminished quantity of the acid is covered by an acid generated from the acid generator included in the water-soluble film **403**. Therefore, deactivation of the acid in the exposed portion **402a** of the resist film **402** can be avoided, so that the resist pattern **406** can be formed in a good shape. In this case, the acid generated from the acid generator included in the water-soluble film **403** is supplied substantially merely to the exposed portion **402a** of the resist film **402**, and therefore, a problem that an unwanted acid is supplied to the unexposed portion **402b** of the resist film **402** can be substantially avoided.

Although the water-soluble film **403** is formed on the resist film **402** in Embodiment 4, the water-soluble film **403** is never dissolved because the immersion lithography is carried out by using the nonaqueous solution **404**.

Although the acid generator included in the nonaqueous solution **403** is triphenylsulfonium nonaflate in Embodiment 4, the acid generator may be a sulfone compound such as bis(phenylsulfonyl)methane; a sulfonate compound such as 2,6-dinitrobenzyltosylate or pyrogallol trimesylate; or a sulfonimide compound such as N-(trifluoromethylsulfonyloxy)succinimide, N-(trifluoromethylsulfonyloxy)phthalimide or N-(trifluoromethylsulfonyloxy)diphenylmaleimide instead.

Furthermore, although the water-soluble film **403** is removed by using the alkaline developer in Embodiment 4, the water-soluble film **403** may be removed by using water before or after baking the resist film **402**.

Although the water-soluble film **403** is made of a polyvinyl alcohol film in Embodiment 4, it may be made of a polyvinyl pyrrolidone film instead.

Although the acid generator is included in the water-soluble film **403** in Embodiment 4, acetic acid, acrylic acid or formic acid may be included instead in the water-soluble film **403**. In such a case, the content of the acid may be several wt%.

EMBODIMENT 5

A pattern formation method according to Embodiment 5 of the invention will now be described with reference to FIGS. **6A** through **6D**.

First, a negative chemically amplified resist material having the following composition is prepared:

Base polymer: poly((norbornene-5-methylenecarboxylate) – (maleic anhydride)) (wherein norbornene-5-methylenelcarboxylate : maleic anhydride = 50 mol% : 50 mol%) ... 2 g

Crosslinking agent: 1,3,5-N-(trihydroxymethyl)melamine ... 0.7 g

Acid generator: trifluorosulfonium triflate ... 0.06 g

Solvent: propylene glycol monomethyl ether acetate ... 20 g

Next, as shown in FIG. **6A**, the aforementioned chemically amplified resist material is applied on a substrate **501** so as to form a resist film **502** with a thickness of 0.20 μm. Thereafter, a water-soluble film **503** made of a polyvinyl alcohol film including 5 wt% of triphenylsulfonium triflate, that is, an acid generator, is formed on the resist film **502**.

Then, as shown in FIG. **6B**, while supplying, between a projection lens **507** and

the water-soluble film **503**, a nonaqueous solution **504** of perfluoropolyether that is circulated and temporarily stored in the solution storage **14** (shown in FIG. **1**), pattern exposure is carried out by irradiating the resist film **502** and the water-soluble film **503** with exposing light **505** of F_2 laser with NA of 0.60 through a mask not shown. Thus, an exposed portion **502a** of the resist film **502** becomes insoluble in an alkaline developer due to the function of the crosslinking agent because an acid is generated from the acid generator therein while an unexposed portion **502b** of the resist film **502** remains soluble in an alkaline developer because no acid is generated from the acid generator therein.

After the pattern exposure, as shown in FIG. **6C**, the resist film **502** is baked with a hot plate at a temperature of 120°C for 60 seconds, and the resultant resist film is developed with a 2.38 wt% tetramethylammonium hydroxide developer (alkaline developer). Thus, the water-soluble film **503** and the unexposed portion **502b** of the resist film **502** are dissolved in the alkaline developer. In this manner, a resist pattern **506** made of the exposed portion **502a** of the resist film **502** and having a line width of 0.09 μm can be formed in a good shape as shown in FIG. **6D**.

In Embodiment 5, since the pattern exposure is carried out after forming the water-soluble film **503** including the acid generator on the resist film **502**, even when the acid generated from the acid generator in the exposed portion **502a** of the resist film **502** flows into the nonaqueous solution **504** and diminishes in quantity, the diminished quantity of the acid is covered by an acid generated from the acid generator included in the water-soluble film **503**. Therefore, deactivation of the acid in the exposed portion **502a** of the resist film **502** can be avoided, so that the resist pattern **506** can be formed in a good shape. In this case, the acid generated from the acid generator included in the water-soluble film **503** is supplied substantially merely to the exposed portion **502a** of the resist film **502**, and therefore, a problem that an unwanted acid is supplied to the unexposed portion **502b** of

the resist film **502** can be substantially avoided.

Although the water-soluble film **503** is formed on the resist film **502** in Embodiment 5, the water-soluble film **503** is never dissolved because the immersion lithography is carried out by using the nonaqueous solution **504**.

Furthermore, although the water-soluble film **503** is removed by using the alkaline developer in Embodiment 5, the water-soluble film **503** may be removed by using water before or after baking the resist film **502**.

Although the water-soluble film **503** is made of a polyvinyl alcohol film in Embodiment 5, it may be made of a polyvinyl pyrrolidone film instead.

Although the acid generator is included in the water-soluble film **503** in Embodiment 5, acetic acid, acrylic acid or formic acid may be included instead in the water-soluble film **503**. In such a case, the content of the acid may be several wt%.

EMBODIMENT 6

A pattern formation method according to Embodiment 6 of the invention will now be described with reference to FIGS. **7A** through **7D**.

First, a positive chemically amplified resist material having the following composition is prepared:

Base polymer: poly((norbornene-5-methylene-t-butylcarboxylate) – (maleic anhydride)) (wherein norbornene-5-methylene-t-butylcarboxylate : maleic anhydride = 50 mol% : 50 mol%) ... 2 g

Acid generator: trifluorosulfonium triflate ... 0.06 g

Solvent: propylene glycol monomethyl ether acetate ... 20 g

Next, as shown in FIG. **7A**, the aforementioned chemically amplified resist material is applied on a substrate **601** so as to form a resist film **602** with a thickness of 0.20 μm. Thereafter, a water-soluble film **603** including an acid polymer of polyacrylic

acid is formed on the resist film **602**.

Then, as shown in FIG. **7B**, while supplying, between a projection lens **607** and the water-soluble film **603**, a nonaqueous solution **604** of perfluoropolyether that is circulated and temporarily stored in the solution storage **14** (shown in FIG. **1**), pattern exposure is carried out by irradiating the resist film **602** and the water-soluble film **603** with exposing light **605** of F_2 laser with NA of 0.60 through a mask not shown. Thus, an exposed portion **602a** of the resist film **602** becomes soluble in an alkaline developer because an acid is generated from the acid generator therein while an unexposed portion **602b** of the resist film **602** remains insoluble in an alkaline developer because no acid is generated from the acid generator therein.

After the pattern exposure, as shown in FIG. **7C**, the resist film **602** is baked with a hot plate at a temperature of 100°C for 60 seconds, and the resultant resist film is developed with a 2.38 wt% tetramethylammonium hydroxide developer (alkaline developer). Thus, the water-soluble film **603** and the exposed portion **602a** of the resist film **602** are dissolved in the alkaline developer. In this manner, a resist pattern **606** made of the unexposed portion **602b** of the resist film **602** and having a line width of 0.09 μm can be formed in a good shape as shown in FIG. **7D**.

In Embodiment 6, since the pattern exposure is carried out after forming the water-soluble film **603** including the acid polymer on the resist film **602**, even when the acid generated from the acid generator in the exposed portion **602a** of the resist film **602** flows into the nonaqueous solution **604** and diminishes in quantity, the diminished quantity of the acid is covered by an acid generated from the acid polymer included in the water-soluble film **603**. Therefore, deactivation of the acid in the exposed portion **602a** of the resist film **602** can be avoided, so that the resist pattern **606** can be formed in a good shape.

In this case, although the acid generated from the acid polymer included in the

water-soluble film **603** is supplied also to the unexposed portion **602b** of the resist film **602**, the quantity of the acid included in the water-soluble film **603** is small, and therefore, the unexposed portion **602b** of the resist film **602** remains insoluble in an alkaline developer.

Although the water-soluble film **603** is formed on the resist film **602** in Embodiment 6, the water-soluble film **603** is never dissolved because the immersion lithography is carried out by using the nonaqueous solution **604**.

Furthermore, although the water-soluble film **603** is removed by using the alkaline developer in Embodiment 6, the water-soluble film **603** may be removed by using water before or after baking the resist film **602**.

Although the water-soluble film **603** includes the acid polymer of polyacrylic acid in Embodiment 6, the water-soluble film **603** may include an acid polymer of polystyrene sulfonic acid instead.